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On the electronic contribution to single molecule surface enhanced Raman spectroscopy

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Abstract : Among the metallic structures supporting single molecule surface enhanced Raman scattering (SERS) this article considers single molecules in junction sites between metallic nanoparticles in small clusters Though high electromagnetic fields can exist in these junctions, they do not increase below gap sizes, where electron tunneling sets in. Following the experimental and theoretical work on DC currents in metal-single molecule-metal systems, a model of resonant optical tunneling via the orbitals of the molecules in the junctions is developed.

Since "canonical SERS" is the "many molecules-many hot sites" ensemble of SM-SERS, we discuss cold-deposited silver films in this respect as ensemble of SM-junction-SERS This is supported by DC resistance measurements during annealing of the cold-deposited films. The individual changes of the DC resistance during exposure of the cold-deposited films to various gases and the simultaneous development of the SERS intensity supports the model of a hybrid field- and electronic SM-SERS in junctions In cold-deposited films, the electronic contribution to SM-SERS is about 3 orders of magnitude One may state, that the field part in junctions enables that Raman signals can be measured, but the electronic part decides, what is seen. (when no intramolecular resonance Raman effect is involved)

Keywords Surface enhanced Raman spectroscopy, electronic contribution, single molecules in junction

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1. Introduction

Optical molecular spectroscopy in condensed matter, especially liquids, matrices or adsorbates at surfaces usually averages over many molecules. The advent of nanofabrication, confocal microscopy, scanning near field optical microscopy (e.g aperture less with resolution of about 10nm [1]), atomic force microscopy has made it possible to observe single molecules, often by fluorescence [2-4]. In the last 8 years also surface enhanced Raman scattering (SERS)[5] has entered the field of nano scale chemical analysis (for instance [6]) and single molecule (SM) spectroscopy. The pioneers of SM-SERS are Katrin Kneipp and coworkers [7, 8] and Shuming Nie and coworkers [9]. Older publications pointing in the direction of SM-SERS are from Hildebrand and Stockburger[10] and Pettinger et al [11, 12], see a review in preparation*.

The phenomenon has mostly been reported with colloidal Ag or Au-particles in solution or fixed at surfaces in most cases for dyes like rhodamine 6G [7, 9, 13-22], crystal violet [8, 23-25], cyanine dye [26] and AzoPTCD [27, 28] in Langmuir Blodgett films, see Figure 1.

SERS has been proven a useful technique in biological research [29-31] and it is supposed that SM-SERS is a new tool for biomedical spectroscopy [32, 33]. An ambitious aim is SM-SERS spectroscopy of single DNA sequencing [34]. SM-SERS of adenine [34-36], adenosine monophosphate [35] haemoglobin [37], tyrosine [38] and horseradish peroxidase (HRP) [39] have been reported, see also the comments of the present author on the interference of graphitic carbon in some of the spectra [40]. Signals from very small quantities of graphitic carbon ("towards single molecule SERS") on SERS-active substrates [41, 42] and on colloidal particles [43] have been seen.

In most cases there is a time dependence of every Raman band intensity, even with on/off behavior, which is called (by

* A Otto, *Single molecule surface enhanced Raman scattering, field- and electronic effects*. Review to be submitted to *J. Raman Spectroscopy*.

most authors) "blinking", and time dependent variations of the band center frequency, which is called spectral diffusion . Both experimental facts, observed at very big dilutions of the observed

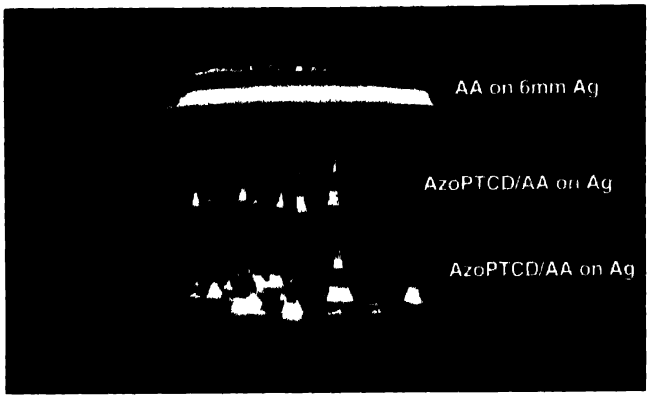


Figure 1. One global image for neat arachidic acid $C_{19}H_{39}COOH$ (AA) Langmuir Blodgett (LB) monolayer (top) and two global images for single molecules of bis(benzimidazo)perylene(AzoPTCD), all recorded at the vibration frequency of AzoPTCD at 1370cm^{-1} The substrate is a silver island film of 6nm mass thickness prepared by vacuum evaporation (10^{-6}Torr) onto a heated substrate at 200°C The area is about 40x40m, the highest peaks correspond to about 600counts (R Aroca, private communication).

molecular species are the hallmarks of single molecule spectroscopy. But blinking of adenine has also been observed from immobilized single Ag particles prepared by using a 10-6M adenine aqueous solution [34]. If all molecules in this solution are adsorbed on the Ag particles, the average number of adenine molecules on a particle would be about 3000. It seems that the time averaged single molecule Raman spectrum is equal to the "many adsorbate-many hot sites" ensemble spectrum [41]. Käll and co-workers [38] reported that single molecule dynamics is even observed in measurements that average over a comparatively large number of colloidal particles and molecules, demonstrating that the small number of "hot" absorption sites, but not the surface concentration of adsorbates, is the decisive limiting factor between SM-SERS and ensemble averaged SERS. Therefore it may have been possible to observe fluctuating intensities and line positions on the simple system CO on an extended Au electrode with confocal Raman spectroscopy by Kudelski and Pettinger [44], see Figure 2. The band at 2117 cm^{-1} is due to CO adsorbed on top of a Au atom, the band at 1956 is from CO in a bridge position between two Au atoms. In contrast to the dyes, resonant Raman scattering of CO is outside the range of the Laser lines in the visible spectral range, nevertheless it seems possible to observe "single molecule"-effects.

In a forthcoming review[1], the author will discuss the SM-SERS observed from single metal particles in an electrolyte and immobilized at a glass surface, from immobilized small clusters and from big particle aggregates in an electrolyte. A further topic will be the evaluation of the enhancement factor, the "blinking", the "chemical effects ", for instance "activation" (whatever the samples or the molecules, an activation is needed, mostly by chloride incubation) and the missing enhancement for water and methanol.

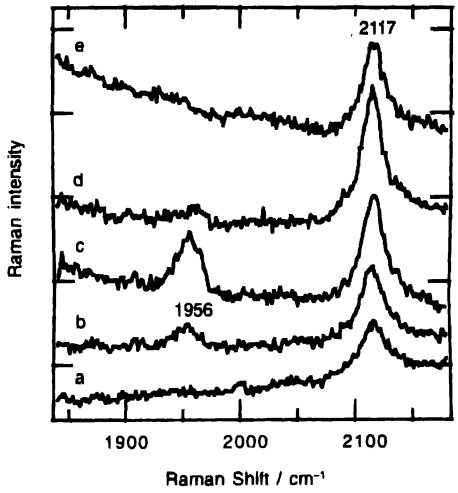


Figure 2. Time series of SERS spectra of CO at roughened Au-electrode. The aqueous electrolyte contains 0 1 M NaCl and is saturated with CO. E= +40 mV vs SCE Recording time 25 s, waiting time between recording 5 s. Roughening was performed in the same electrolyte, but in a different cell having lower ohmic resistance 100 potential cycles were performed from -0.6 V to 1.25 V and back at a scan rate of 50 mV/s The final potential was -0 6 V, at which the electrode was kept for 5 min The electrode was then disconnected and moved to the Raman cell. There are no experimental values for the CO coverage (B.Pettinger, private communication)

The scope of this article is only the discussion of a mixed field- and electronic enhancement mechanism of molecules without resonance Raman effect in the visible spectral range, adsorbed in narrow junction sites in small clusters. Hence, this model does not apply to SM-SERS involving single metal particles and intra-molecular resonant Raman scattering, though there exist convincing experiments for SM-SERS also in these systems*.

In section 2) the experimental evidence for the junction sites given in the literature will be presented.

2. Evidence for SM-SERS from junction sites

According to Brus and coworkers [16, 18, 22] Rayleigh scattering and direct AFM examination show that huge cross sections for single molecules occur in compact, nonfractal aggregates of several individual ~50nm silver nanocrystals, (see the atomic force microscopy pictures in Figure 3). In Ref. [22], the integrated fluctuating Rh 6G SERS signal emitted normal to the glass substrate, on which the small clusters were immobilized, was measured simultaneously for two orthogonal directions, see the time dependence of the intensities in Figure 4. The polarizations S and P denote polarizations perpendicular and parallel to the plane of incidence of the laser beam. The latter was at 514.5 nm and grazing incidence, and *P*-polarized. (In a 2-dimensional projection *S* in Figure 4 means that the electric

vector of the incoming Laser beam and of the outgoing Stokes emission are parallel, *P* means that the Stokes electric vector is rotated by 90° with respect to the electric vector of the Laser beam. Both components fluctuate simultaneously, and the ratio remains the same for a given aggregate. Now a representative SERS active aggregate is rotated by a varying angle Θ around an axis normal to the glass plate, centered in the cluster. The polarization directions are unchanged in the laboratory frame. A non fluctuating polarization parameter $\rho = (I_{SS} - I_{SP})/(I_{SS} + I_{SP})$ is observed, where I_{SS} (I_{SP}) is the intensity for outgoing *S*(*P*) polarization (see Figure 5) with a characteristic $\cos 2\Theta$ variation. In contrast, the Rayleigh scattered light does not fluctuate and is always polarization preserving (*S*-polarized).

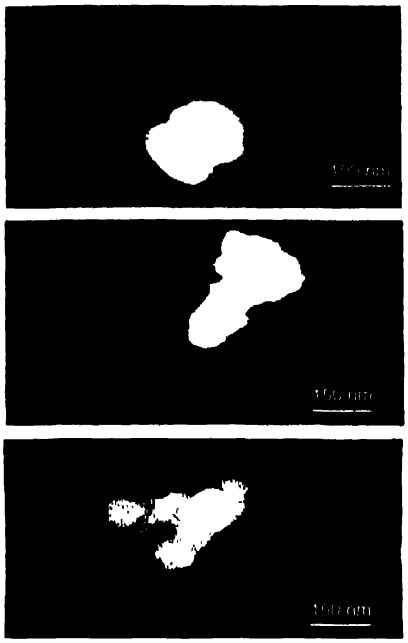


Figure 3. AFM images of 3 different SERS-active Ag aggregates prepared by incubating a Ag colloid with 10 mM NaCl and 2 nM Rh 6G The heights of the aggregates ranged from ~50 to ~200 nm

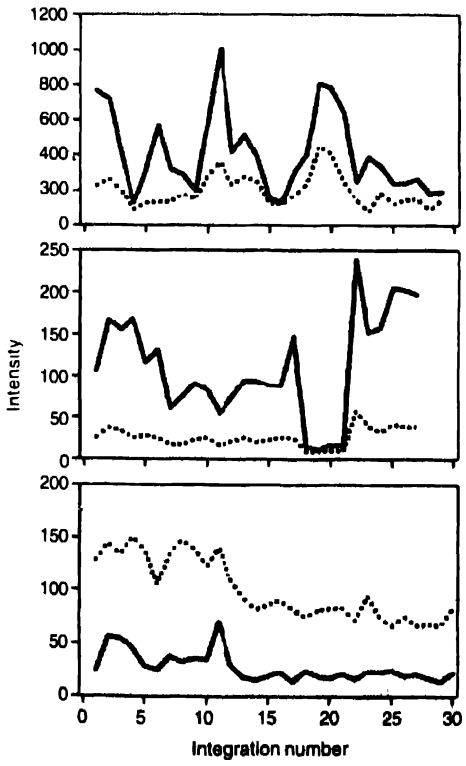


Figure 4. Time dependence of the intensities of the *S*-(solid) and *P* (dotted) polarized Raman scattering from 3 different SERS active aggregates The scattering is excited by 514.5nm, *S*-polarized light at glazing incidence; all the Stokes (and anti-Stokes)shifted light contributes to the signal. The integrations are 1s long and taken continuously at 2s intervals

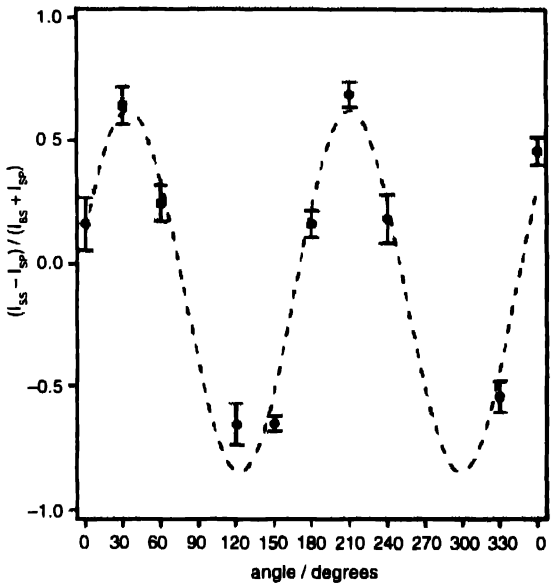


Figure 5. Angle dependence of the polarization parameter r for a representative SERS-active aggregate. The scattering is excited by 514.5 nm, *S*-polarized light; all the Stokes (and anti-Stokes) shifted light contributes to the signal. The integrations are 1 *s* long and taken continuously at 2 *s* intervals Ten integrations are taken at each angle, with 30° increments. A polarization parameter equal to 1 indicates that the scattering is completely polarized and -1 indicates that it is completely depolarized. The error bars represent standard deviations.

This is explained with the heuristic and tutorial model of a cluster of C4 - symmetry, see Figure 6. When the source of Raman scattering is in the gap or junction between two spheres, the two spheres are antennas for both the incoming as well as the emitted light. They work very well, when the direction of polarization is parallel to the connecting direction between the centers of the two spheres and is inefficient for the direction perpendicular to the connecting line. I_{ss} for junctions1and 3 would therefore show a $(\cos\Theta)^2$ dependence, but the angular dependence would be washed out by the $\sin\Theta^2$ dependence of the junctions 2 and 4, provided the source of radiation in the 4 junctions has the same strength. This is the reason , why the Rayleigh scattered light is not dependent on Θ and keeps the polarization of the laser light. Now it is assumed, that only one junction is occupied by an Rh 6G molecule. Then irrespective in which junction 1-4 the molecule resides, the depolarization *r*

should display the same cos2θ pattern. That means, that the pattern is not changed, if 2,3,or 4 junctions were populated with Rh6G. If only one junction is populated, the I_{xx} SERS-component would show a $(\cos\theta)^2$ or $(\sin\theta)^2$ angular pattern, which would disappear if for instance junctions 1 and 2 were populated. This measurement is not described in [22], probably because of the blinking problem. However the authors state that the model predicts that the Rayleigh intensity is independent of θ, whereas the SERS intensity varies strongly with θ, consistent with the earlier measured absence of correlation between Rayleigh and Raman intensities for arbitrary directions [16, 18]. A local C_3 trimer cluster is probably as likely as a C_4-cluster. In this case, if only one junction is populated, and one assumes, that the antenna effect for a molecule in the junction can be considered like in a dimer cluster of the two nearly touching spheres, one can expect again a $\cos 2\theta$ pattern for the depolarization ratio, but not when 2 or all three junctions of the trimer are occupied.

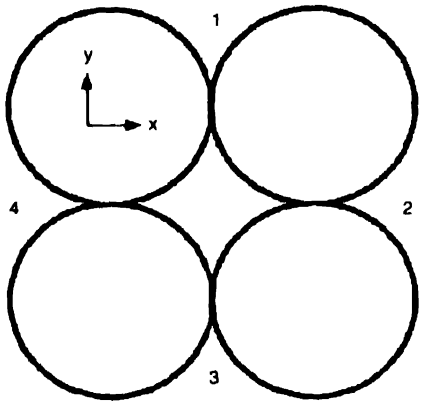


Figure 6. Schematic representation of the difference between Rayleigh and Raman scattering from SERS-active aggregates. The Rayleigh scattering is delocalized over the whole aggregate which, in this example, is isotropic due to the 4-fold axis of symmetry (Formally, an axis of symmetry of order three or higher ensures that the tensor is isotropic in the plane perpendicular to that axis) Conversely, the Raman scattering is highly localized at one of the junctions, which is highly anisotropic

So it seems, that the observed depolarization pattern in Figure 5 is "robust" concerning the arrangement of the second nearest particles of a "SERS-active" molecule in a junction, when only a minority of junction sites is populated by the same "SERS"-active molecular species.

The excitation mechanism of the vibrations in the junction cannot be inferred from these results on the "antenna-affect", it may be a field enhancement or a hybrid field- and electronic mechanism. This will be discussed in the next section.

3. SM-SERS in junction sites, theory and discussion

(a) On the contribution of field enhancement in narrow gaps :

The local field intensity enhancement at the junction site or at the narrow gap between spherical silver particles has been calculated [18, 37, 45, 46], following older theoretical work [47-50]. The Finite Difference Time Domain (FDTD)-method, which allows to calculate local field enhancement in irregular structures has also been applied to junction sites [25, 51]. As a rule of thumb, the enhancement of the field intensity has been squared to obtain the field enhancement of Raman scattering by molecules at the center position of the gap or junction, see one example in Figure 7. The result of the calculation can be well approximated by the simple equation

$$\frac{D+d}{d}$$

with obvious notation. This corresponds to the compression of the difference of the electric potential between the centers of the spheres (in the absence of the spheres) into the gap of the junction. The volume of the hot spot is the product of the width d of the gap between the spheres of radius r with the area of the lateral extension of the hot spot rd [45].

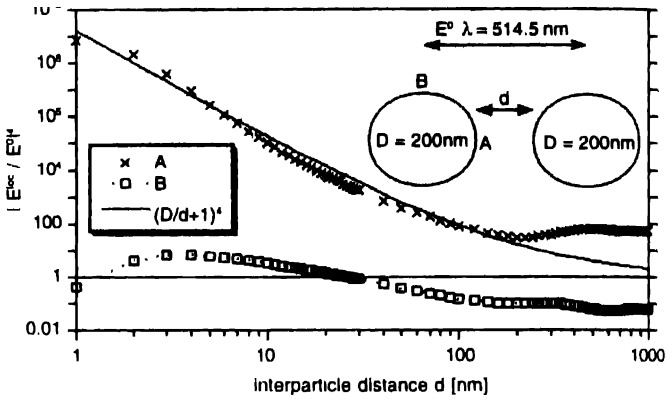


Figure 7. Calculated SERS enhancement-factor for a Ag dimer system in the parallel polarization configuration as a function of interparticle separation *d*. The calculations have been performed for two positions, *A* and *B*, located 0.5 nm from the surface of one of the spheres and at Laser wavelength 514.5 nm. The electrostatic model of interparticle coupling illustrated in Figure 1 can quantitatively explain the dramatic increase in enhancement that occurs when $D/d > 1$. Note that the enhancement at the off axis position *B* is almost always below unity (*i.e.* no enhancement)

In this local field enhancement model, only those molecular vibrations do contribute to the spectrum, which have *zz*-components of the Raman tensor in the Euclidian coordinate frame defined by the 2 spheres (line from center to center defines the *z*-direction). Irrespective of the orientation of the molecule, vibrational modes which have no diagonal components of the Raman tensor in the molecular axial system would not show up Variations of the orientation and diffusion in and out of the hot spot might explain the blinking.

Without exception, all calculations of the field enhancement have been performed with the model of local optics, in which a surface of a metal and a dielectric is described by an infinitively sharp boundary, separating the metal with the complex dielectric constant $\varepsilon(\omega)$ and for instance vacuum with the dielectric constant $\varepsilon_{vac} \equiv 1$. In the following, this will be called the infinite barrier model, because electrons are not allowed to leak out towards the metal side, as they do in reality, see Figure 8.

When using the infinite barrier model at the distances given in Figure 7 one can consider the gap between the two spheres

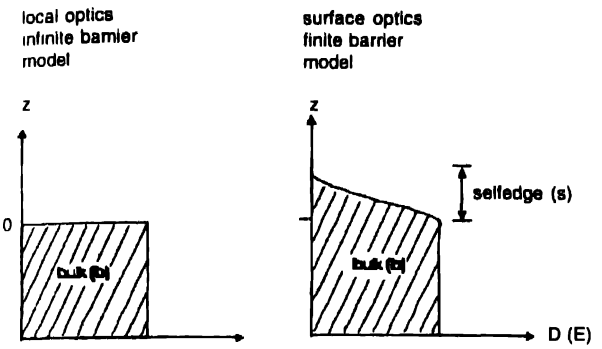


Figure 8. Density $D(E_F)$ of electrons at the Fermi energy versus the direction z normal to the interface between metal and external medium, left infinite barrier model, right finite barrier model (schematic).

is a capacitor. In this case the optical current density $J_{optical, metal}$ in the spheres, given in local optics by

$$\underline{J}_{optical\ metal}(\omega) = \sigma_{optical}(\omega)\,\underline{E}_{metal}(\omega) \qquad (1)$$

with $\sigma_{optical}(\omega) = -i\varepsilon_0\omega(\varepsilon(\omega)-1)$

and $\underline{E}_{optical,metal}$ being the electrical field strength in the metal spheres is going over continuously into the displacement current within the gap between the two spheres

$$\underline{J}_{optical,gap}(\omega) = -i\omega\varepsilon_0\underline{E}_{optical\ gap}$$

like in a capacitor. Giving up the infinite barrier model, the density $n(\varepsilon_F, d/2)$ of electrons at Fermi energy, propagating in the spheres in direction of the axis between the spheres, in the middle of the empty gap of width d between the spheres can be easily approximated assuming an abrupt barrier of the height of the work function Φ :

$$\frac{n(\varepsilon_F, d/2)}{n(\varepsilon_F)} = 4e^{-\frac{\sqrt{2m\Phi}}{\hbar}d}. \qquad (2)$$

For silver with $\Phi = 4.5$ eV and $d = 1$nm one obtains for this ratio a value of about 7.7×10^{-5}

At $d = 0.5$nm, the ratio is already 0.0157 and at a distance of the diameter of one silver atom (0.288nm), where an ethylene molecule would still fit into the gap between the spheres [52] it is already 17.5%. Therefore when decreasing the gap the displacement current is more and more replaced by the electron tunneling current and the high enhancement values proportional to the 4th power of the local field will come down. Therefore the very high calculated enhancements below a gap size of 0.5-1.0nm are unphysical. A realistic theory would bring the field enhancement of SERS to values much lower than 10^{10} at a gap of 0.228nm opening.

(b) On electronic enhancement :

The idea of the author is, that the optical electronic currents between the two spheres of the narrow junction, as discussed in section 5 may run "through" a molecule adsorbed in the junction. Before developing this further, one should have a look at the better understood situation in the DC case.

DC currents through metal-single molecule-metal junctions :

These junctions have been realized in break junctions [53-55] and between the tip of a scanning tunneling microscope (STM) and a metallic substrate [56, 57]. In any case the directed current (DC) voltage characteristics has been measured, characteristically dependent on the molecule. There are 3 ingredients which determine the contribution of a molecular orbital of the single molecule to the current: (i) its energy position with respect to the Fermi levels of the metals, (ii) the bridging extent, depending whether the orbital is extended or localized on the molecule, (iii) its coupling to the leads (the metal on both sides) of the junction [58]. Not necessarily do the highest occupied orbital ("hole conduction") or lowest unoccupied orbital ("electron conduction") dominate the transport properties, also nonfrontier orbitals can and do contribute in special cases [58]. The question how optical currents would flow through the molecule and how they couple to the molecular vibrations is given in the next subsection.

Optical currents through metal-single molecule-metal junctions[59] :

For a qualitative discussion, one can profit from considering the DC case. There will be coherent optical currents at the Laser frequency by resonant tunneling through the different molecular orbitals. Electrons in empty orbitals or holes in filled orbitals exert bonding or antibonding forces between the atoms of the molecule, which lead to distortions of the molecules, corresponding to distortions as they occur in some of the elementary vibrations of the molecule. This yields the selection rules of SERS, which are different from the normal Raman selection rules, see for instance the comparison of SERS of C_6H_6 and C_6F_6 [60]. The overall SERS process of a single molecule in a junction is a coherent process, the phases of the incoming laser light, the coupled surface plasmon modes of the two particles, the phase of the excited vibration and of the Stokes light are locked to each other during the Raman scattering process.

The orientation of the molecule in the narrow junction with respect to the nearest neighbor metal atoms on both metal particles decides whether and which orbitals are open for the current (see [59] for the example of C_2H_4 in the junction). In this way changes of orientation or very small scale jumps can induce blinking, fluctuation of the ratios between different SERS bands and spectral diffusion, irrespective of the cause of the orientation changes, be they thermal, *e.g.* by cooling or Laser

enhancement intensity is weaker than that of the other modes [67], approximately the same as for the analogue mode in ethane.

The initial submonolayer Raman scattering intensity of the CC-breathing mode of benzene is enhanced by about a factor of 6×10^4, which is composed of a field enhancement of about 190 and an electronic enhancement of about 315, see Figure 10 in [68]. If the field enhancement of SERS in the case of ethylene adsorption will stay at about 200, the electronic enhancement of the ν(CC) mode of ethylene will be around 1000.

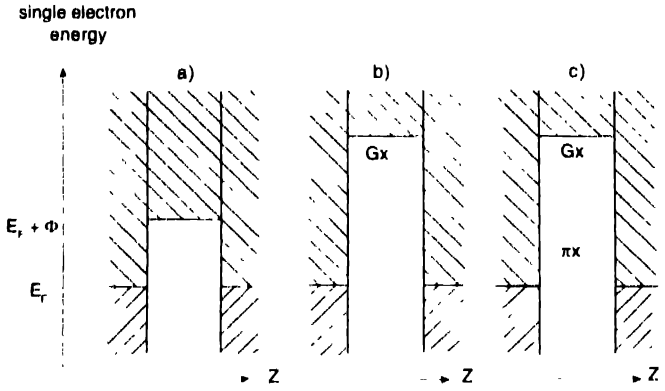


Figure 14. Energy of single electron basis functions at a narrow tunnel junction (a) without an adsorbate (b) with a saturated hydrocarbon adsorbate and (c) with unsaturated hydrocarbon adsorbate. Areas hatched from left down to right up: continuum states, filled; Areas hatched from right down to left up: continuum states, unfilled. E_f is the Fermi level, ϕ is the work function, σ^* , π^* are unfilled orbitals and z is the direction from grain to grain of the cold-deposited silver

In summary, in the cold- deposited films, the molecules which influence the resistance display an additional "chemical enhancement " of about 3 orders. The mechanism can be described as electron tunneling across narrow junctions via intermediate orbitals of the molecules adsorbed at the sites of narrow junctions. That is less than a quarter of all the sites in the cold-deposited films. In this sense, SERS from cold-deposited films is the ensemble averaged case of SM-SERS at junction sites between two metal-nanoparticles. It is not absolutely certain, that junctions in cold-deposited films and in immobilized nanoclusters are identical. The overlap of metallic states and molecular orbitals increases exponentially with "squeezing" the molecule in the junction , but the electrical field will decrease with "squeezing". In SM-SERS the field enhancement of Raman scattering by the resonating nano-particles is much higher than in a cold-deposited film, which to my opinion explains in first order the big difference of enhancement between cold-deposited films and nano clusters[2].

[2] Of course, a discussion on field resonances in cold-deposited films, described by fractals [69] should follow at this point. I think an effective medium model describes these films better. I leave this to a future discussion, the impatient reader may find some hints in [70]. Of course, theory has to respect experimental results or indicate what may have been done wrong. the experimental value of the average contribution of field enhancement to SERS in cold-deposited silver films at 514.5 nm excitation is about 190.

If this correspondence is valid, then also the inelastic background in "canonical"SERS must have an analogue in SM-SERS.

(b) On the inelastic background :

The inelastic background of cold-deposited films is Raman scattering by excitation of electron hole pairs, not luminescence [71], see Figure 15. It can be fitted to a simple model, whose details are given in [71].

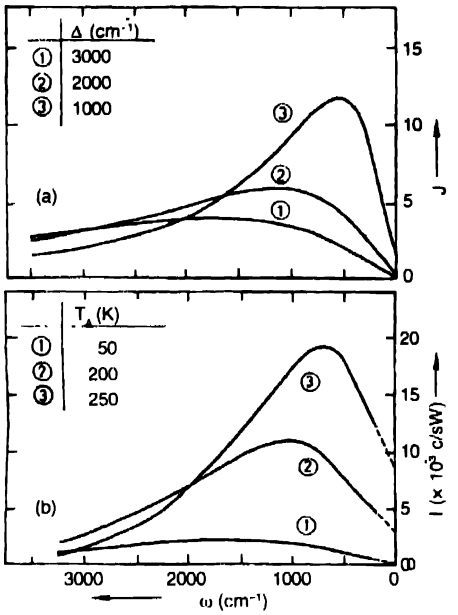
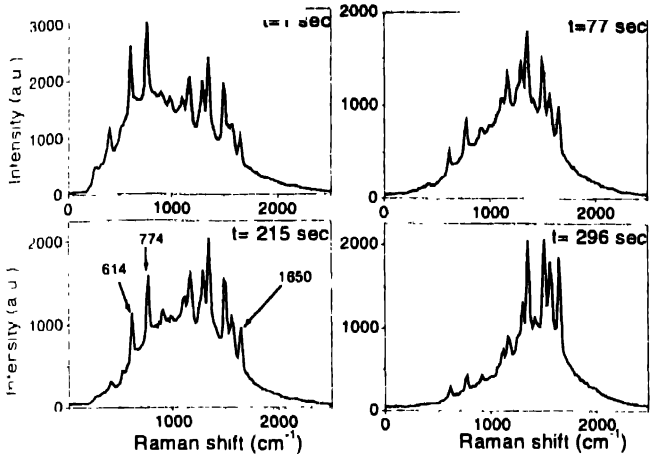


Figure 15. Calculated joint density of states J(ω) of intraband transitions within bands of Lorentzian density with half width Δ and maximum weight at the Fermi level, units are arbitrary. The temperature is taken to be 50K. (b) Electronic Raman spectra at 40K after annealing at temperatures T_A, noise omitted

In SM-SERS, Weiss and Haran[20] and Brus and company [18, 21, 22] mention an inelastic background. Weiss and Haran state, that the intensity of the background has an intimate connection to the Raman bands above it, as its shape fluctuates simultaneous with them, see Figure 16.

It is gratifying to read in [18]: "All strong SERS signals (of R6G at 514.5nm excitation) contain both continuum and sharp lines; occasionally a signal 10x weaker is observed consisting only of continuum. When the excitation wavelength was changed from 514.5nm to 632.8nm, 10 of these particles showed significant Stokes shifted intensity. However 9 of these 10 particles showed only continuum emission without any evidence of R6G Raman lines.." and in [21]: "A key observation is that before halide treatment the SERS spectrum often contains a broad background and weak signals from citrate or its degradation products, but no detectable R6G signal. R6G suddenly replaces the citrate spectrum and appears over the background in a simple step". However , the Brus- group stated recently [22], in contrast to ref [18], cited above: "In our

experiment, only those aggregates that show R6G Raman also show continuum scattering". It seems that one needs more solid evidence.



gure 16..Sample spectra taken from a SERS trajectory of a single R6G olecule adsorbed on a silver nanocrystal and illuminated with a laser wer of 18 W/cm^2 Each spectrum, collected in 1 second, is labeled with relative time in the sequence Variations in the intensities of individual bration bands and of the background are evident, and are especially ted for the two lowest frequency bands seen here, at 614 and 774 cm^{-1}, ich can be assigned to C-H bending vibrations

According to K Rowlen (private communication) it is not rrect to state the "absence of adsorbates" in the SM speriments, because it is nearly impossible to design a colloid speriment in which there is "nothing" on the colloid surface ven in vacuum). But it appears that Ag colloids "blink" respective of the nature of the adsorbate.

Summary

Many experimental results in SM-SERS are not completely nderstood, as will be outlined in a forthcoming review by the uthor[1] This paper is restricted to the experimental indications nd the possible explanations for enhanced Raman scattering single molecules, which have no intramolecular electronic xcitation in the visible range, in so-called junction sites between lver nanoparticles in small clusters (not withstanding the SM-l RS results for single nanoparticles). The recent results from he group of Louis Brus on a constant depolarization ratio r in pite of strong blinking and the cos2 Φ variation of r, when the anocluster is rotated by the angle Φ is a strong indication for unctions However it does not follow, that the intensity hancement is a pure field-effect. Firstly, there is the firm undisputable fact, that the theoretical models based on local ptics fail for narrow gaps, because electron tunneling between he silver nanoparticles cannot be neglected. This will stop the pectacular increase of the local electric field in the limes of a losed gap.

Secondly there can be resonant optical tunneling via the rbitals of the molecule in the gap, in analogy to the well documented DC case in metal-single molecule-metal experiments. This interaction , but not the local field , will determine the SM-SERS selection rules.

"Canonical SERS" is ensemble averaged SM-SERS. This article gives strong arguments that the cold-deposited silver films contain an ensemble of junctions sites, based on DC resistance measurements. The resistance caused by tunneling through gaps between crystalline grains of unexposed cold-deposited silver films decreases analogous to the surface roughness factor. Molecules in the films at junction sites decrease or increase the resistance, depending on the possibility of resonant tunneling. Only the subgroup of molecules which affects the DC resistance contributes to the SERS spectrum. The average electronic enhancement of the Raman intensity is about 3 orders. With due caution this may perhaps also be expected in SM-SERS with small silver clusters. Certainly the electromagnetic field enhancement is higher by several orders in junction sites between nanoparticles with strong surface plasmon resonance's. Nevertheless I state: The field effect enables that Raman spectra of single molecules are observable, the electronic effect determines, what is seen.

Unexposed cold-deposited films display a background which is Raman scattering by single electronholepair excitation. To check the case of the cold-deposited films as an ensemble of junction sites, one needs information on the background in SM-junction-SERS. Although it has been reported that SM-SERS shows always a background, blinking with the SM-SERS, the literature is not unequivocal concerning the existence of a background without an adsorbate signal.

Many of the SM-SERS experiments have been performed with dyes, sometimes in the laser frequency area of the resonance Raman (RR) effect. This is outside the scope of this article. The most acute investigated system, to which the electronic model of this article should apply, is CO on a roughened gold electrode, see Figure 2 above. Nevertheless, charge transfer effects may also be important for dyes. Weiss and Haran [20] took SM-SERS spectra of Rhodamine 6G at a Laser wavelength of 532nm in the range of RR scattering [10]. They believe, that the definite connection of the fast fluctuating intensity of the C-H bend bands and the changes in the shape of the diffuse background in this spectral area, see Figure 16, may have the origin in a molecule-surface charge transfer phenomenon.

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